DE 3524890

[Patent entitled process for preparation o low-molecular-weight olefins]

Translated from German by the Ralph McElroy Co., Custom Division
P.O. Box 4828, Austin, Texas 78765 USA

Code: 417-55059

97BC0321

Reference #1

Dr. Dieter Weber
Klaus Seiffert

Patentanwälte

3524890

PM97019

Dipl.-Chem. Dr. Dieter Weber · Dipl.-Phys. Klaus Seiffert
Postfach 6145 · 6200 Wiesbaden

D-6200 Wiesbaden 1

Gustav-Freytag-Straße 25
Telefon 0 61 21/37 27 20 - 37 25 80
Telegrammadresse: Willpatent
Telex: 4-186 247
Telekopierer Gr. III 0 61 21/37 21 11

Postscheck: Frankfurt/Main 67 63-602
Bank: Dresdner Bank AG, Wiesbaden,
Konto-Nr. 276 807 00 (BLZ 510 800 60)

German Patent Office
Zweibrückerstrasse 12
8000 Munich

Date: July 11, 1985
We/Wh
512 407 DP

Agency of Industrial Science & Technology
1-3, Kasumigaseki 1-chome, Chiyoda-ku
Tokyo, Japan

Process for preparation of low-molecular-weight olefins

Priority: Japanese Patent Application
No. 59-146 289 of July 14, 1984

Claims

[1]1. Process for preparation of low-molecular-weight olefins, characterized by the fact that methanol and/or dimethyl ether and recycled hydrocarbons are contacted in the gas phase with a zeolite catalyst, and in this manner methanol and/or dimethyl ether are converted to low-molecular-weight olefins, and the total amount or a part of the reaction product remaining after removal of the ethylene and propylene formed is used as the recycled hydrocarbons.

2. Process as per Claim 1, characterized by the fact that as zeolite catalyst, an alkaline-earth metal-containing zeolite catalyst, an alkaline-earth metal-modified alkaline-earth metal-containg zeolite catalyst, a ZSM zeolite catalyst impregnated with an alkaline-earth metal, and/or an alkaline-earth metal-modified ZSM zeolite catalyst are used.

3. Process as per one or several [sic] of Claims 1 and 2, characterized by the fact that as zeolite catalyst, an alkaline-earth metal-containing zeolite catalyst and/or an alkaline-earth metal-modified alkaline-earth metal-containing zeolite catalyst are used.

[1] [Translator's note: The awkward grammar and inaccuracies in the translation follows the original document]

4. Process as per one or several of Claims 1-3, characterized by the fact that a mixture of fresh raw materials consisting of methanol and/or dimethyl ether with recycled hydrocarbons is contacted with the zeolite catalyst in a temperature range of 300-650°C.

5. Process as per one or several of Claims 1-4, characterized by the fact that the hourly weight-based space velocity of a mixture of fresh raw material consisting of methanol and/or dimethyl ether with [sic] recycled hydrocarbons is adjusted to a range of 0.12-36 per hour.

6. Process as per one or several of Claims 1-5, characterized by the fact that the weight-based mixing ratio of the recycled hydrocarbons to fresh raw material consisting of methanol and/or dimethyl ether is adjusted to 0.1-0.9:1.0.

7. Process as per one or several of Claims 1-6, characterized by the fact that the fresh raw material consisting of methanol and/or dimethyl ether with recycled hydrocarbons is contacted with the zeolite catalyst at a pressure of 0.1-100 atm.

8. Process as per one or several of Claims 1-7, characterized by the fact that as recycled hydrocarbons, fractions after the aromatic compounds have been removed from the remaining reaction product are used.

9. Process as per one or several of Claims 1-8, characterized by the fact that as recycled hydrocarbons, aliphatic hydrocarbons with 4-8 carbon atoms are used.

The invention pertains to a process for preparation of low-molecular-weight olefins, and especially to a process for preparation of ethylene and propylene from methanol and/or dimethyl ether.

In past years, efforts have been made to establish a reliable source for crude oil. Japan imports 99% of the crude oil used in the country from abroad, so that it is an important matter to effectively utilize coal, natural gas, and the like in Japan. In addition, there were demands that an industrial process be found for a preparation of organic compounds such as olefins, paraffins, and aromatics from methanol which [in turn] was obtained from methane, CO, etc.

It is now generally known in the industry that silica, aluminum oxide, aluminosilicate, or the like can be used as catalyst in the conversion of hydrocarbons.

In the seventies, Mobile Oil Co. developed a zeolite catalyst of the ZSM-5 type as a form-selective catalyst for preparation of hydrocarbons with a qualitatively high-grade gasoline base of methanol or dimethyl ether (US-PS 3 702 886). This zeolite has excellent properties such that its compositional ratio of SiO_2/Al_2O_3 can be intensively controlled in addition to having a high heat resistance in contrast to conventional zeolites. If the properties of the zeolite are fully exploited, it is also possible to control the conversion reaction from methanol or dimethyl ether in such a manner that a primary product is obtained that consists of low-molecular-weight olefins.

However, in order to produce ethylene and propylene with high selectivity, a high reaction temperature is needed, so that even a zeolite catalyst of the ZSM-5 type does not have an adequately long-lasting activity, and loses its activity in a short period of time.

The present inventors dedicated themselves to studies to develop a catalyst with a longer-lasting activity than catalysts

of the ZSM-5 type, and the result of this was that they succeeded in developing an alkaline-earth metal-containing zeolite catalyst (Japanese Laid-Open Patent No. 59-97523) and an alkaline-earth metal-modified alkaline-earth metal-containing zeolite catalyst (Japanese Laid-Open Patent No. 59-105 530).

These catalysts have a longer useful life than catalysts of the ZSM-5 type at high reaction temperatures. For example, whereas a catalyst of the ZSM-5 type has a useful life of 10 h or less at 550°C under the precondition that the liquid hourly space velocity (LHSV) is 2 per hour, the alkaline-earth metal-containing zeolite catalyst has a useful life of 50-200 h, and the alkaline-earth metal-modified alkaline-earth metal-containing zeolite has a useful life of 300-700 h.

However, demands have recently been made that a process for preparation of low-molecular-weight olefins for obtaining ethylene and propylene be developed with higher selectivity [and], for economic reasons, to obtain more stable operation over a longer period of time by extending the useful life of the catalyst. For this reason, the inventors studied the reaction conditions for preparation of low-molecular-weight olefins, especially ethylene and propylene, from methanol and/or dimethyl ether in detail in addition to [making] efforts to improve the zeolite catalyst; the result of this was that they succeeded in meeting the above requirements by improving the reaction conditions.

It is a first goal of the invention to obtain a process for producing low-molecular-weight olefins, especially ethylene and propylene, from methanol and/or dimethyl ether with high selectivity at low reaction temperatures.

It is a second goal of the invention to obtain a process for producing low-molecular-weight olefins, especially ethylene and propylene, from methanol and/or dimethyl ether, which makes stable operation possible over a long period of time.

According to the invention, methanol and/or dimethyl ether together with recycled hydrocarbons are brought into contact with the zeolite catalyst in the gas phase in order to convert methanol and/or dimethyl ether to low-molecular-weight olefins, the resulting ethylene and propylene are removed from the reaction products, and thereafter the total or a portion of the residual reaction product is used as recycled hydrocarbons.

With regard to the catalyst to be used according to the invention, a catalyst is preferred that leads to formation of a multitude of aromatic hydrocarbons, such as a BTX of 10% or less, based on the amount of product, since BTX is considered a precursor to coke. In addition, a catalyst is preferred that produces a ratio of low molecular weight C_2-C_5 olefins of 50% or more, based on the amount of product.

As zeolite catalysts that fulfill these requirements, especially the above-indicated alkaline-earth metal-containing zeolite catalyst and the alkaline-earth metal-modified alkaline-earth metal-containing zeolite catalyst, and moreover, a zeolite catalyst of the ZSM type impregnated with alkaline-earth metal (Japanese Laid-Open Patent No. 58-234 747) and an alkaline-earth metal-modified zeolite catalyst of the ZSM type that was prepared by simple mixing of a ZSM catalyst with an alkaline-earth metal-containing compound in the solid state can be mentioned.

The alkaline-earth metal-containing zeolite catalyst (Japanese Laid-Open Patent No. 59-97523) is a calcined product that was prepared using a raw material with a composition

corresponding to a m lar ratio of SiO_2/Al_2O_3 of 12-3000, a molar ratio of OH^-/SiO_2 of 0.02-10, a molar ratio of H_2O/SiO_2 of 1-100, a mole ratio of tetrapropylammonium compound to SiO_2 of 0.02-2, and an atomic ratio of alkaline-earth metal to Al of 0.03-300, and subsequent hydrothermal treatment of the raw material at a temperature in a range from 80-200°C and has a composition of the formula $aM_2O \times bM'O \times Al_2O_3 \times cSiO_2 \times nH_2O$ (wherein M is an alkali metal atom and/or hydrogen, M' is an alkaline-earth metal, a is 0-1.5, b is 0.2-40 (wherein a + b is greater than 1), c is 12 to 3000, and n is 0-40).

The alkaline-earth metal-modified alkaline-earth metal-containing zeolite catalyst (as per Japanese Patent Application No. 59-105 530) is a catalyst that was prepared by modification of the alkaline-earth metal-containing zeolite catalyst (Japanese Laid-Open Patent No. 59-97523) by treatment of same with an alkaline-earth metal-containing compound in solution or in the solid state, wherein the compound was converted in that at least 0.25 wt% of the alkaline-earth metal, calculated as the metal, is taken up by the zeolite or mixed with it.

The zeolite catalyst of the ZSM type impregnated with an alkaline-earth metal (Japanese Patent Application No. 58-234 747) is a catalyst prepared by modification of a ZSM catalyst by treatment of same with an alkaline-earth metal-containing compound in solution so that the catalyst contains the compound in an amount of at least 0.25 wt%, based on the weight of the catalyst, recalculated as alkaline-earth metal.

As ZSM zeolites, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, and ZSM-48 can be mentioned.

In addition, as alkaline-earth metal-modified ZSM zeolites, [the following] can be mentioned: ZSM-5 (US-PS 3 702 886), ZSM-11

(US-PS 3 709 979), ZSM-12 (US-PS 3 832 449), ZSM-23 (US-PS 4 076 842), ZSM-35 (US-PS 4 016 245), ZSM-38 (US-PS 4 046 859), and ZSM-48 (US-PS 4 397 827).

In addition, alkaline-earth metal-containing compounds that are to be mixed with the ZSM catalysts contain salts, oxides, hydroxides, and the like of various alkaline-earth metals. As salts of an alkaline-earth metal, various inorganic and organic salts of alkaline-earth metals can be mentioned; and carboxylates such as acetates, [and] carbonates, nitrates, and phosphates thereof are preferred.

The mixing ratio of alkaline-earth metal-containing compound to ZSM zeolite catalyst is at least 0.25 g (as the recalculated value of the compound as alkaline-earth metal based on 100 g of the ZSM zeolite catalyst); and 1-35 g (similarly calculated and referred to the same basis as above) is preferred.

In the invention, the contacting of methanol and/or dimethyl ether and the recycled hydrocarbons with the above-indicated catalyst, i.e., the conversion reaction of methanol and/or dimethyl ether into low-molecular-weight olefins, occurs at a temperature of 300-650°C, preferably from 400-600°C, more strongly preferred, from 450-550°C. In addition, the hourly weight-based space velocity of raw material is 0.1-20/h, preferably 1-10/h. In this, fresh raw material means newly introduced methanol and/or dimethyl ether. The hourly weight-based space velocity of the reaction gas that consists of fresh raw material and recycled hydrocarbons is 1.2-1.8-fold that of the raw material and is 0.12 to 36/h, preferably 1.2 to 18/h.

The weight-based mixing ratio of the recycled hydrocarbons to fresh raw material is usually 0.1 to 0.9:1, preferably 0.3 to 0.7:1.

In addition, the above-indicated conversion reaction of methanol and/or dimethyl ether into low-molecular-weight olefins is done under pressure conditions of 0.1-100 atm, preferably 0.5-10 atm.

Furthermore, in the invention, the reaction heat is decreased and diluted [sic] with the aid of recyled hydrocarbons as will be described later, and it is also possible to dilute the mixture of methanol and/or dimethyl ether with recycled hydrocarbons with steam, inert gas, nitrogen, argon, carbon dioxide, flue gas after removal of impurities such as residual oxygen and sulfur dioxide, or the like and then to pass the diluted gas over the catalyst; the use of diluted gas is generally preferred.

The significance of recycled hydrocarbons for the process of the invention will be described below.

As indicated above, in order to prepare hydrocarbons with a low-molecular-weight olefin base from methanol and/or dimethyl ether, it is advantageous to increase the reaction temperature as high as possible. However, an increase in the reaction temperature rapidly decreases the useful life of the catalyst. For example, in a temperature range usually used for preparation of olefins from methanol and/or dimethyl ether, the useful life of the catalyst is usually decreased approximately by half when the reaction temperature is increased by approximately 50°C, and it becomes impossible to continue stable operation over a longer period of time. If operation in this process is forcibly continued, the catalyst reactivity decreases significantly, and when the catalyst with extremely decreased activity is treated for regeneration, its activity cannot be recovered.

The inventors d voted themselves to study with regard to a method of increasing the selectivity for ethylene and propylene while maintaining a constant reaction temperature, and as a result of this, it was found that the yield of ethylene and propylene could be increased by recycling the remaining reaction product after removal of ethylene and propylene, totally or in part, into the reaction system. The conversion reaction of raw materials, methanol and/or dimethyl ether, into low-molecular-weight olefins is not inhibited by recycling of the remaining reaction products, and as a result of this, it becomes possible to prepare ethylene and propylene with high selectivity at a reaction temperature of 50-100°C lower than if the remaining reaction products had not been recycled, so that the useful life of the catalyst is extended.

In addition, recycling of the remaining reaction product is very effective in preventing local overheating of the catalyst layer. The exchange reaction of methanol to dimethyl ether is a pronouncedly exothermic reaction, and the conversion of dimethyl ether into olefins such as propylene and the like is also an exothermic reaction so that removal of reaction heat becomes an important matter, and inadequate removal of reaction heat leads to formation of superheated sites in the catalyst layer which produced a decrease in the useful life of the catalyst.

Since, on the other hand, preparation of low-molecular-weight olefins by decomposition of hydrocarbons is a strongly endothermic reaction, a strongly exothermic reaction from preparation of olefins from methanol is in part compensated for by the decomposition reaction of the recycled hydrocarbons so that temperature control of the catalyst layer is made easier and more advantageous.

As indicat d above, in the invention, the total amount or a part of the reaction product reamining after ethylene and propylene have been removed from the reaction product is used as the hydrocarbon to be recycled or recirculated.

However, since aromatic compounds such as BTX and the like cause coking of the catalyst [sic] and have a high value as raw materials for the chemical industry, it is preferred that they be removed from the recycle fraction. Moreover, hydrocarbons with a high number of carbons are capable of causing coking and forming tar-like substances in the reaction; suitable hydrocarbons for recycling are therefore aliphatic hydrocarbons with 4 to 8 carbon atoms.

In addition, since higher hydrocarbons with carbon numbers greater than 6 are not converted to ethylene and propylene unless they are cracked to a high degree, and they produce a strong coating of the catalyst and are capable of being subject to cyclicization and aromaticization, they are not suitable for [obtaining] high yields of ethylene and propylene, so that the more suitable hydrocarbons for recycling are aliphatic hydrocarbons with 4-6 carbon atoms. Butylene itself is a low-molecular-weight olefin and becomes a raw material for synthesis of solvents such as sec-butyl alcohol, methyl ethyl ketone, butylcellosolve, antioxidants, pesticides, surfactants, and the like used in various applications so that it does not need to be recycled.

In addition, components with a carbon number of 4 and greater which are removed from the fractions to be recycled can be subjected to hydrogenation and subsequent thermal cracking or steam cracking to convert them to low-molecular-weight olefins if this is needed.

In the process of th invention, the product stream consists of steam obtained by dehydration of methanol and/or dimethyl ether, hydrocarbons, and unreacted raw materials; suitable adjustment of the reaction conditions can increase the ratio of low-molecular-weight olefins such as ethylene and propylene in the hydrocarbons. The steam and the hydrocarbon products are separated and purified by generally known methods.

As indicated above, the total amount or a part of the reaction products remaining after ethylene and propylene have been removed from the reaction product are recycled or recirculated and mixed with methanol and/or dimethyl ether. As a result of this, the local overheating of the catalyst layer is prevented as a result of endothermic decomposition reactions of the remaining reaction products added to the reaction system, and the reaction can be done with high selectivity at low reaction temperature, which extends the useful life of the catalyst.

Furthermore, preventing local overheating increases the yield of ethylene and propylene and, while the yields of ethylene and propylene by the conventional method under reaction conditions of 500°C and an hourly liquid space velocity of 2/h is 45 to 50%, yields in the process of the invention can be increased to 65%. In addition, stable operation can continue over a long period of time via the process of the invention.

Examples of the invention are given below.

Example 1

Preparation of an alkaline-earth metal-containing zeolite catalyst and alkaline-earth metal-modified alkaline-earth metal-containing zeolite catalyst (by the impregnation method)

1.14 g aluminum nitrate nonahydrate and 1.34 g calcium acetate monohydrate were dissolved in 90 g water in order to produce Liquid A. 60 g water glass (Cataloid SI-30, product of Shokubai Kasei Co., SiO_2: 30.5%, Na_2O: 0.42%) were dissolved in 40 g water in order to produce Liquid B. Liquid B was added to Liquid A with vigorous stirring, and thereafter 1.26 g sodium hydroxide dissolved in 20 g water were added to the mixture. In addition, 8.11 g tetrapropylammonium bromide dissolved in 30 g water were added to the resulting mixture with stirring, and stirring was continued approximately 10 min more in order to obtain an aqueous gel mixture. The SiO_2/Al_2O_3 molar ratio in the charge of raw material was 200.

The aqueous gel mixture was introduced into an autoclave with an interior volume of 300 mL and treated hydrothermally at 160°C for 18 h under its own pressure with stirring at 500 rpm. The resulting reaction product was separated into solid components and liquid components by centrifugation. The solid components were adequately washed with water and then dried for 5 h at 120°C. Subsequently, the solid components were treated in air at 520°C for 5-20 h. 0.6N HCl was mixed with the resulting calcined zeolite in a mixing ratio of HCl to zeolite of 15 mL: 1 g and the mixture was then stirred at room temperature for 24 h. Thereafter, the zeolite was adequately washed with water at room temperature, and after drying at 120°C, was calcined for 5 h

in air at 520°C in order to convert it to the H form. It had an Si content of 43.2%, an Al content of 0.42%, and a Ca content of 0.70%.

5 g of the thus-obtained Ca-containing zeolite were mixed with an aqueous solution produced by dissolving 3.14 g $Ca(CH_3COO)_2 \times H_2O$ in 10 mL water. The mixture was held at 80°C for 20 h and then evaporated and dried in a dryer at 100-110°C. Thereafter, the mixture was calcined in air for 2 h at 200°C and additionally for 18 h at 500°C; a Ca-modified Ca-containing zeolite was obtained.

Example 2

Preparation of an alkaline-earth metal-modified alkaline-earth metal-containing zeolite catalyst (by the mixing method)

5 g of the Ca-containing zeolite prepared as per Example 1 were mixed in the solid state with 1.8 g of a powder obtained by calcining $Ca(CH_3COO)_2 \times H_2O$ at 500°C and subsequent pulverization of the calcined substance in a mortar, and in this manner a Ca-modified Ca-containing zeolite was obtained by the mixing method.

Example 3

Preparation of a ZSM zeolite catalyst impregnated with alkaline-earth metal

1.14 g aluminum nitrate nonahydrate were dissolved in 90 g water in order to produce Liquid A and 60 g water glass (Cataloid

SI-30, product of Shokubai Kasei Co., SiO_2: 30.5%, Na_2O: 0.42%) were dissolved in 40 g water in order to produce Liquid B. Liquid B was added to Liquid A with vigorous stirring, and thereafter 1.26 g sodium hydroxide dissolved in 20 g [water] were added to the mixture, and subsequently 8.11 g tetrapropylammonium bromide dissolved in 30 g water were added. The resulting mixture was additionally stirred approximately 10 min and an aqueous gel mixture was obtained. The SiO_2/Al_2O_3 molar ratio in the charge of raw material was 200.

The aqueous gel mixture was introduced into an autoclave with an interior volume of 300 mL and treated hydrothermally at 160°C for 18 h under its own pressure with stirring at 500 rpm. The reaction mixture was separated into solid components and liquid components by centrifugation. The solid components were adequately washed with water, dried for 5 h at 120°C, and then treated in air at 520°C for 5 to 20 h. Thereafter, 0.6N HCl was mixed with the resulting calcined crystalline aluminosilicate in a mixing ratio of HCl to aluminosilicate of 15 mL:1 g and the mixture was then stirred and treated [sic] at room temperature for 24 h. Thereafter, the aluminosilicate was adequately washed with water at room temperature, dried at 120°C, and subsequently calcined in air at 520°C for 5 h; In this manner, ZSM-5 of the H type (Si: 43.1 wt%, Al:0.45 wt%) was converted to the H form.

5 g of the thus-obtained ZSM-5 of the H type (SiO_2/Al_2O_3 = 200) were mixed with an aqueous solution produced by dissolving 3.14 g $Ca(CH_3COO)_2 \times H_2O$ in 10 mL water. After holding the mixture at 80°C for 20 h, the mixture was evaporated and dried in a dryer at 100-110°C. Thereafter, the dried mixture was calcined in air for 2 h at 200°C and additionally for 18 h at 500°C; a Ca-modified ZSM-5 was obtained in this manner.

Example 4

Preparation of an alkaline-earth metal-modified zeolite catalyst of the ZSM by mixing of zeolite catalyst of the ZSM type with [an] alkaline-earth metal-containing compound

5 g of the ZSM-5 zeolite catalyst prepared in Example 3 were mixed with 1.55 g of a powder obtained by calcining $Ca(CH_3COO)_2{\times}H_2O$ at 500°C and subsequent pulverization of the calcined substance in a mortar, and in this manner a Ca-modified ZSM-5 zeolite catalyst was obtained.

Comparative Example 1

Case in which hydrocarbons were not circulated and only methanol was used

A powder of the zeolite prepared in Example 1 was pelletized at a pressure of 400 kg/cm^2 subsequently the resulting pellets were comminuted into particles of uniform particle size of 10-20 mesh. 2 mL of the zeolite particles were packed into a test tube with an interior diameter of 10 mL. Liquid methanol was introduced into an evaporator at a rate of 2 mL/h (3.2 g/h) (although the [conversion] reaction was a gas [phase reaction], the hourly liquid space velocity was 2/h when the raw material feed is expressed as liquid phase). As indicated above, the methanol introduced was vaporized in an evaporator and mixed there with argon in an amount of 40 mL/min and the mixture was introduced into the test tube at approximately standard pressure in order to perform the reaction at a reaction temperature of

500°C. The analyses of the reacti n products were done with a gas chromatograph. The experiment [with] only methanol as raw material for the preparation of low-molecular-weight olefins was repeated [several times] under the same reaction conditions since the experiment constituted a standard for evaluation of the effect of the process of the invention. The average value of the results of these repeated experiments and also the minimum and maximum values of the results are shown in Table I in order to indicate the range of fluctuation.

<u>Example 5</u>

Gaseous 1-butene was added to the raw material used in Comparative Example 1 in an amount of 4.3 mL/min, and the resulting mixed gas was used instead of recycling a portion of the reaction product into the reaction system due to the limitations of the reaction apparatus. The reaction of the mixed gas was done in the same apparatus and under the same conditions as in Comparative Example 1, and the analysis of the reaction product was done by the same method as in Comparative Example 1. The results are shown in Table I. This experiment corresponds to a 1.4048-fold raw material feed rate, based on carbon, [when compared to] Comparative Example 1. This value is nearly the same as the raw material feed rate for the case where hydrocarbons with 4-6 carbon atoms obtained in Comparative Example 1 are recycled in order to feed them into the reactor together with fresh raw material, and specifically, based on carbon. The ratio of ethylene (C_2') plus propylene (C_3') in the reaction product, based on carbon, decreased from 45.75% in Comparative Example 1 to 41.90%. However, if one takes into account the 1.4048-fold increase of the feed rate, based on carbon, then the yield of C_2'

plus C_3' increases 1.29-fold, based on carbon, when compared to Comparative Example 1. Assuming that the added 1-butene is a portion of the reaction product, if the selectivity for C_2' plus C_3', based on carbon, is determined, the recycled part is 58.86%.

Since both methanol and dimethyl ether are starting materials in the process for preparation of low-molecular-weight olefins as per the invention, in the calculation of the selectivity, dimethyl ether deriving from methanol can be considered as unreacted raw material.

Example 6

Instead of adding gaseous 1-butene in amounts of 4.3 mL/min [as] in Example 5, isobutene in an amount of 4.8 mL/min was added and the reaction of the resulting mixed gas was done in the same manner as in Example 5. The results are shown in Table I. An interpretation of the experimental results can be done in the same manner as in Example 5.

In Examples 5 and 6, the reaction product is recycled in an amount corresponding to approximately 40-45% of the amount of fresh raw material, based on carbon. However, in this case, the amount of C_4-C_6 components in the reaction product, based on carbon, exceeds the amount of added butene, based on carbon. This fact shows that the circulating amount of C_4-C_6 components can be further increased if operation is continued.

Example 7

The reaction was done in the same manner as in Example 6 with the exception that the feed rate of isobutene was increased to 11.4 mL/min. The results are shown in Table I.

Example 8

The conversion was done by the same method as in Example 6 but with the exception that the feed rate for isobutene was increased to 16.5 mL/min. The results are shown in Table I.

The amount of isobutene added in Example 7 corresponds to 107.25% of the amount of fresh raw material, based on carbon, and the corresponding amount in Example 8 corresponds to 154.71% of the amount of fresh raw material, based on carbon. In this case, the amount of C_4-C_6 components in the reaction product, based on carbon, is less than the added amount of isobutene, based on carbon. The results of Examples 5-8 show that the amount of suitable hydrocarbons that can be recycled in doing the process of the invention automatically approaches a certain value if operation is continued. Naturally, the operating conditions can be adjusted in such a manner that the recycled amount is held at a value that is different from the value to which [the reaction] automatically adjusts itself.

Example 9

The conversion was done by the same method as in Example 5 but with the exception that instead of 1-butene addition at a rate of 4.3 mL/min [as] in Example 5, 1-hexene was added in liquid form at a rate of 2 mL/h. The results are shown in Table I.

Example 10

The conversion was done by the same process as in Example 9 but it was done with the exception that instead of addition of 1-hexene in an amount of 2 mL/h [as] in Example 9, 1-octene was added in liquid form in an amount of 2 mL/h. The results are found in Table I.

The addition of 1-hexene in liquid form in an amount of 2 mL/h in Example 9 corresponds to a recycle of hydrocarbons in an amount of 90.95% of that of the fresh raw material, based on carbon; and addition of 1-octene in liquid form at an amount of 2 mL/h in Example 10 corresponds to a recycle of hydrocarbons in an amount of 110.96% of that of the fresh raw material, based on carbon. The proportion of ethylene and propylene formed in the reaction product, based on carbon, and the hypothetical selectivity of ethylene and propylene, based on carbon, when the hydrocarbon addition is taken as hydrocarbon recycling are compared with one another for Examples 7, 9, and 10, which all have nearly the same amount of recycle, based on carbon. The results of this that the proportion decreases in the sequence: Example 9, Example 7, and Example 10; and the selectivity decreases in the sequence: Example 7, Example 9, and Example 10. However, the range of fluctuation among these three examples is not so large, and the selectivity values for them are all extremely notable compared to the selectivity values in Comparative Example 1. The proportion of high-boiling hydrocarbons of unknown structure that are formed increases in the sequence: Example 7, Example 9, and Example 10, which shows that the amount of heavy oil formed increases and the danger of

catalyst worsening and coke formation increases with an increase of the carbon number of the recycled hydrocarbons.

Table I

		1 Vergleichsbeispiel nur Methanol 2			3 Beisp. 5 4,3 ml/min 1-Buten zuges	3 Beisp. 6 4,8 ml/min 1-Buten zuges	3 Beisp. 7 11,4 ml/min 1-Buten zuges. 4	3 Beisp. 8 16,5 ml/min 1-Buten zuges	3 Beisp. 9 2 ml/h 1-Hexen zuges. 5	3 Beisp. 10 2 ml/h 1-Okten zuges. 6
		min.	M mittel	max.						
7 Ausbeute (%), bezogen auf Kohlenstoff	$CO+CO_2$	0.04	0.20	0.35	0.19	0.03	0.02	0.01	0.02	0.04
	CH_4	0.25	0.62	0.92	0.11	0.18	0.12	0.11	0.16	0.23
	C_2H_4	3.95	4.53	5.15	5.46	4.74	3.85	3.46	3.55	2.69
	C_2H_6	0	0	0.01	0	0	0	0	0	0.03
	C_3H_6	38.15	41.22	42.57	36.44	38.72	34.49	30.91	36.05	31.92
	C_3H_8	0.25	0.33	0.50	0.57	0.41	0.37	0.34	0.34	0.28
	C_4H_8	15.43	17.02	18.31	17.70	19.12	19.41	19.86	16.90	15.19
	C_4H_{10}	0.73	0.94	1.22	1.28	1.55	2.11	2.43	1.01	0.98
	C_5H_{10}	8.21	9.72	10.24	7.20	8.81	10.20	11.02	9.37	9.42
	C_5H_{12}	3.54	3.73	3.98	3.79	3.89	4.01	4.11	3.48	3.43
	C'_6+C_6*1	6.09	6.73	6.99	5.49	6.36	7.11	7.56	6.62	6.43
	Methanol	0.64	0.79	0.94	0.73	0.08	0	0	0.50	0.57
	Ethanol	0.03	0.28	0.79	0.17	0	0	0.05	0	0
	DME*2	0	0.01	0.12	0.01	0.01	0	0.01	0.01	0
	B.T.X	0.83	1.39	1.76	1.27	1.32	1.56	1.56	1.19	0.78
	UKHC*3	10.33	12.49	17.23	19.59	14.78	16.75	18.57	21.00	28.01
	Total		100.00		100.00	100.00	100.00	100.00	100.00	100.00
8	$C'_2+C'_3$*4(A)		45.75		41.90	43.46	38.34	34.37	39.60	34.61
Beschickung*5(B)			1.00		1.4048	1.4492	2.0725	2.5471	1.9025	2.1096
Ap.select.*6			45.75		58.86	62.98	79.46	87.54	75.34	73.01
Ef.select.*7			46.12		59.30	63.04	79.46	87.55	75.73	73.43

Key: 1 Comparative Example, only methan 1
2 Average
3 Example
4 mL/min 1-butene added
5 2 mL/h 1-hexene added
6 2 mL/h 1-octene added
7 Yield based on carbon
8 Feed

*1 Total amount of C_6 olefins and C_6 paraffins

*2 Dimethyl ether

*3 High-boiling hydrocarbons of unknown structure

*4 Total amount of ethylene and propylene

Feed *5 Feed, based on carbon, when Comparative Example 1 is used as standard

Ap.select *6 The calculated total amount of hypothetical selectivity for ethylene and propylene when the hydrocarbon addition is taken as the recyle amount of a part of the reaction product (A x B)

Ef. select

*7 Selectivity with respect to methanol and dimethyl ether in the reaction product corrected as the unreacted raw material